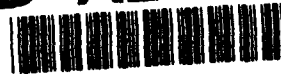


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**Direct Dimer-by-dimer Identification of Clean and Monohydride Dimers on
the Si(001) Surface by Scanning Tunneling Microscopy**

by

Y. Wang, M. Bronikowski, and R.J. Hamers

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Department of Chemistry
University of Wisconsin-Madison
Madison, WI 53706

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Direct dimer-by-dimer identification of clean and monohydride dimers on the Si(001) surface by scanning tunneling microscopy

Yajun Wang, Michael J. Bronikowski and Robert J. Hamers*

Department of Chemistry

University of Wisconsin

1101 University Avenue, Madison, WI 53706

ABSTRACT

Atomic resolution images of clean Si(001)-(2x1) and the monohydride phase, Si(001)-(2x1)H were investigated using scanning tunneling microscopy at various sample-tip bias voltages. At a sample-tip bias of -1.9 V, each dimer of the monohydride phase shows two protrusions 3.3 Å apart separated by a minimum 0.12 Å deep, while clean dimers show a single protrusion per unit cell. Monohydride dimers appear lower than "clean" dimers, with apparent height differences ranging from 1.9 Å at -1.6 V to 0.65 Å at -3.0 V sample bias. An analysis of the apparent height and spatial distribution of tunneling current within each dimer can be used to unambiguously discriminate between clean dimers, monohydride dimers, and vacancy defects. This methodology is applied to study the distribution of hydrogen on Si(001) surfaces during chemical vapor deposition using disilane, revealing segregation of the monohydride into nearly isotropic islands.

*Author to whom correspondence should be addressed

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INTRODUCTION

The interaction of hydrogen with silicon surfaces has been extensively studied due to its technological importance in chemical vapor deposition of Si, Ge, and Si:Ge alloys, and as a model system for understanding adsorption on semiconductor surfaces. In CVD processes, hydrogen can be deposited through decomposition of precursors such as SiH_4 ¹⁻³, GeH_4 ⁴ or Ge_2H_6 ⁵, and Si_2H_6 ³. Since the early observation of the $\text{Si}(001)-(2\times 1)\text{H}$ monohydride structure^{6, 7}, the adsorption and desorption of hydrogen on $\text{Si}(001)$ has been studied by a large number of surface science techniques including low-energy electron diffraction⁷, ultraviolet photoemission spectroscopy(UPS)⁶, infrared spectroscopy^{8, 9}, high-resolution electron energy loss spectroscopy (HREELS)¹⁰, temperature programmed desorption (TPD)^{11, 12} and secondary-ion mass spectroscopy (SIMS)¹³. Atomic-resolution scanning tunneling microscopy images of the ordered monohydride phase, $\text{Si}(001)-(2\times 1)\text{H}$, in which each surface silicon atom has one adsorbed hydrogen atom, were first obtained by Hamers, et al.¹⁴⁻¹⁶ by exposing the $\text{Si}(001)$ surface to NH_3 . More recently, Boland¹⁷⁻²² has used scanning tunneling microscopy (STM) to study the behavior of hydrogen with silicon surfaces prepared by dosing with atomic hydrogen and with disilane (Si_2H_6). He observed that at low hydrogen coverages, the hydrogen atoms tend to pair onto a single dimer (thereby forming a dimer of the monohydride structure), instead of remaining randomly distributed on the surface. Lin, et al.²³ also claim to have observed small islands of monohydride phase produced by thermal dissociation of disilane.

Recently, the identification and the observation of monohydride on epitaxial silicon islands has been a subject of some controversy; while Boland¹⁸ and Lin, et al.²³ each reported observing islands of pure

monohydride on a "clean" substrate during thermal dissociation of disilane, a more detailed study by Wang, et al.²⁴ showed that the epitaxial islands consist of "clean" silicon. Additionally, while Hamers, et al.¹⁴⁻¹⁶ reported that filled-state topographs of the Si(001)-(2x1)H monohydride structure shows two maxima per unit cell (near the locations of the Si-H bonds), neither Boland nor Lin, et al. were able to reproduce this, and Boland²² suggested that it might arise from a tip artifact. The controversy surrounding proper identification of the monohydride structure has motivated us to study in more detail the Si(001)-(2x1)H monohydride structure.

EXPERIMENTAL

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of less than 10^{-10} torr. The STM consists of a single-tube scanner mounted at the end of a Burleigh "Inchworm"; all feedback and inchworm control electronics were home-made²⁵. N-type Si(001) wafers oriented to within 0.5° (Virginia Semiconductor) were used. Clean Si(001)-(2X1) surfaces were prepared by degassing at 950 K for 10-12 hours, and then annealing to 1425K for several seconds while maintaining the pressure near 1×10^{-10} torr. After cooling to room temperature (about 30 min), the samples were exposed to 10% Si₂H₆ in He (Voltaix, Inc) through a leak valve. Because the only significant impurity in disilane is silane and the latter has a much smaller sticking coefficient^{26,27}, disilane can be used without further purification. By controlling the exposure to disilane and controlling the annealing temperature, the degree of hydrogenation and the size of the monohydride islands could be varied. All images were acquired in the constant current

mode using tunneling currents between 0.1 and 1.0 nA and a range of bias voltages between 1.2 and 3 Volts at negative sample bias (probing filled surface states).

RESULTS and DISCUSSION

Fig. 1a shows a region of Si(001) after exposure to 0.6 Langmuirs disilane and annealing to 660 Kelvin, imaged with a sample bias of -3.0 Volts. In this figure, the dimer rows of the substrate run from lower left to upper right, and the epitaxial dimers formed by dissociation of disilane form rows only a single dimer wide, running from upper left to lower right. On the substrate terrace, there are large regions comprising approximately 20% of the total area which appear dark. Although it might be thought at first that these dark areas are vacancies, suitable adjustment of the contrast shows that they are not. rather. Dimers within the "dark" regions show two main differences from the other "clean" dimers. First, the dimers in the dark regions appear 0.8 \AA lower than the "clean" dimers. Secondly, each of the "dark" dimers shows two clear, well-resolved protrusions within each unit cell, while the "clean" dimers show only a single maximum at the center of the dimer bond. This can be seen more clearly in figure 1b, which shows an enlarged view of the rectangular region outlined in fig. 1a. By adjusting the contrast such the normal dimers saturate the grayscale and appear totally white, the apparent splitting of the monohydride dimers into two well-resolved protrusions can be observed; several examples of this can be observed by the arrows in fig. 1b. Thus, we find that the monohydride dimers appear lower than "clean" dimers and also show a different spatial distribution of tunneling

current within the unit cell, with a secondary minimum at the center of the Si-Si dimer bond.

Figure 1c shows the changes more quantitatively. Here, we show the height contour measured along the line between the two arrowheads in fig. 1a. This height contour cuts across two epitaxial islands and shows that these islands are separated by a vertical displacement of $1.3 \pm 0.1 \text{ \AA}$, consistent with the 1.36 \AA monatomic step height on the Si(001) surface. On the lower terrace, the contour passes over several dimers of the monohydride structure and several "normal" dimers, showing that for dimers within a single atomic plane, those consisting of H-Si-Si-H are approximately 0.8 \AA lower than those of Si=Si. Additionally, the height profile shows that the spatial distribution of tunneling current for the monohydride phase shows two well-resolved maxima separated by $3.3 \pm 0.1 \text{ \AA}$, near the anticipated locations of the H atoms (for example, over the monohydride dimer at a lateral distance of 70 \AA), while for the clean Si=Si dimers there is a single maximum at the center of the Si=Si bond. The observed separation of $3.3 \pm 0.1 \text{ \AA}$ separation between maxima also agrees with the previous measurements by Hamers, et al.¹⁴⁻¹⁶ using STM and Shoji, et al.²⁸ using low-energy recoil-ion spectroscopy. Using the 110° H-Si-Si bond angle measured by Shoji, et al.²⁸ and bond distances²⁹ of $d_{\text{Si-Si}} = 2.36 \text{ \AA}$ and $d_{\text{Si-H}} = 1.53 \text{ \AA}$ leads to a 3.42 \AA separation between two hydrogen atoms in H-Si-Si-H. The net result is that filled-state STM images of the monohydride surface show two well-resolved protrusions in each unit cell while the Si=Si dimers appear like bean-shaped ovals, as in fig. 1a and 1b.

In order to understand the difference in appearance of "clean" and "monohydride" dimers, it is important to understand the basic symmetry

of STM images of the clean surface and the electronic structure of dimers with two adsorbed hydrogen atoms, H-Si-Si-H, which is the basic structural unit of the Si(001)-(2x1)H monohydride surface. The geometric and electronic properties of the clean Si(001) surface and of the Si(001)-(2x1)H monohydride surface and how these properties are manifested in occupied state STM images were delineated by Hamers, et al.^{14-16, 30, 31}. A simple molecular orbital approach can be used quite successfully to qualitatively understand the changes arising from dimerization and from adsorption of simple atomic species. Figure 2 shows a simplified energy diagram for two silicon atoms of the bulk-truncated surface before 2(a) and after 2(b) dimerization, while 2(c) depicts the changes in electronic structure produced by adsorption of two hydrogen atoms; this structure 2(c) is referred to as the Si(001)-(2x1)H monohydride structure.

In the bulk-truncated Si(001) surface, each surface Si atom has two sigma bonds to the bulk substrate (labeled " σ_s ") and two half-filled, sp^3 -hybridized dangling bonds (labeled " sp^3 "). As originally noted by Appelbaum and co-workers³², the formation of a dimer can be understood as a rehybridization of these four sp^3 -hybridized "dangling bonds" into molecular orbitals of the dimer which can be described as σ , π , σ^* , and π^* in nature. The σ bond is quite strong but the π bond is weak, with the result that the energy difference between the occupied π state and the unoccupied π^* state is small, less than 1 eV. In STM images at negative sample bias electrons must tunnel out of occupied states of the sample, so that the STM images primarily reflect the spatial distribution of the occupied π state (lying 0.6 eV below E_F), while images at positive sample bias reflect the spatial distribution of the unoccupied π^* antibonding state (lying about 0.2 eV above E_F). The π orbital is essentially bean-shaped,

although the calculations predict an increased density of occupied states directly above the individual Si atoms for distances within a few Å of the dimer. Because the STM tip is about 8-10 Å from the dimers, however, STM images typically show only a bean-shaped structure with a maximum at the center of the Si=Si bond. Because the π^* orbital has a node at the center of the Si=Si dimer bond, the state density there drops to zero and the tip must push toward the sample to achieve constant tunneling current. As a result, at positive sample bias clean Si=Si dimers appear like two well-resolved atoms, while at negative bias they appear bean-shaped as the tip follows the contours of the empty and filled electronic states, respectively³¹.

Adsorption of two hydrogen atoms onto a dimer produces the H-Si-Si-H "monohydride" structure. As depicted in fig. 2c, this can be understood as a breaking of the weak π bond and the formation of strong $\sigma_{\text{Si-H}}$ bonding and $\sigma^*_{\text{Si-H}}$ antibonding orbitals which lie farther from E_F than the corresponding π and π^* orbitals of the clean Si=Si dimers. Indeed, Hamers, et al.¹⁴⁻¹⁶ showed that the energy of the Si-H antibonding state is approximately 1.5 eV above E_F , while photoemission experiments³³ place the Si-H bonding state 4.7 eV below E_F . Thus, the density of both occupied and unoccupied states near E_F is significantly reduced by hydrogen adsorption into the monohydride phase. This is indeed consistent with the STM images at negative bias (as presented here and in the previous publications^{14-16, 24}) and with the work of Boland²¹ at positive sample bias. At both positive and negative bias, dimers of the monohydride structure appear lower than clean dimers because the density of states near the Fermi energy is reduced by hydrogen adsorption.

A remaining point of controversy is the presence or absence of a secondary minimum at the center of the H-Si-Si-H monohydride dimer bond. While such a minimum was reported in the first monohydride observation by Hamers, et al.¹⁴⁻¹⁶, later studies did not always observe this minimum. Boland²² even claimed that there was no such minimum and that its previous observation was a "tip artifact". Our results do not support this interpretation.

Boland²² argued that STM images of the monohydride structure could not show a splitting at bias voltages between -1 and -3 V, because the Si-H bonding states at 4.7 eV³³ below E_F are not accessible, and tunneling can therefore only occur through bulk valence band states. However, we believe that existing electronic structure calculations may not properly take into account all the rehybridizations which occur upon H adsorption. Indeed, the very fact that adsorbed H-Si-Si-H groups still appear 0.2 Å higher (at -2.0 V bias, for example) than the underlying terrace indicates that there is *some* state density accessible to the STM, irrespective of its detailed origin. More recent semi-empirical self-consistent calculations on silicon clusters by Badziag and Verwoerd³⁴ in fact reproduce our experimental results very well, showing a clear dip between the atoms for the H-Si-Si-H monohydride, but not for the clean dimers.

Another possible explanation for the discrepancies between our work and that of Boland^{21, 22} and Lin, et al.²³ is the possibility of artifacts due to dull or asymmetric tips. We consistently find that STM tips which are sharp enough to resolve individual dimers on two adjacent terraces of the Si(001) surface, and which are symmetric enough to show consistent corrugation amplitudes parallel and perpendicular to the dimer rows on these two terraces, *always* show a splitting along the center of the H-Si-Si-H

bond for the monohydride structure. Neither the study by Boland^{21, 22} nor the study by Lin, et al.²³ showed clear resolution of the individual dimers even on a single terrace, suggesting that atomically-sharp tips might be required to observe the dimer splitting.

While the height difference alone might be sufficient to distinguish clean and monohydride dimers in some instances, observation of the dimer splitting is important to *reliable* identification of the monohydride. At both positive and negative bias, monohydride dimers appear 1-1.5 Å lower than clean dimers; this height change is close to the 1.36 Å depth of a vacancy (equal to the Si(001) step height)³⁵, so that monohydride dimers and vacancies will *both* appear as depressions of nearly the same depth. As shown below, unless the internal structure within the unit cell can be resolved, these two cannot easily be distinguished. We further note that when imaging unoccupied states, both clean- and monohydride structures show two maxima per unit cell, and so distinguishing between the structures must be done solely on the basis of the changes in apparent height with the positive sample bias images. At positive sample bias, then, distinguishing monohydride dimers from vacancies is expected to be difficult in all circumstances.

With an understanding of how to identify dimers of clean and monohydride Si(001), we can study the spatial distribution of hydrogen on the substrate and islands terraces on a dimer-by-dimer basis. For example, fig. 3a shows a surface prepared by exposing Si(001) to 0.6 L Si₂H₆ at 300 K, and then annealing to 660 Kelvin. This image also contains a monatomic step; the higher terrace is in the lower right portion of the image, and the lower terrace is in the upper left part of the image. Each large terrace shows both clean- and monohydride dimers produced by

decomposition of disilane on the surface followed by diffusion of hydrogen and nucleation into monohydride regions. Additionally, small epitaxial islands are observed, which tend to be long and narrow, perpendicular to the dimer rows of the substrate dimer rows. A close examination of these epitaxial islands likewise shows that some of the dimers are bean-shaped, and some are about 1.2 \AA lower and appear to be split, indicating that they are the monohydride phase. This can be seen more clearly in fig. 3b, which is an enlarged view of the rectangular region outlined in fig. 3a. In fig. 3b, the arrows show the boundaries of an epitaxial "dimer string" 9 dimers long in which 5 dimers are the monohydride phase and 4 dimers (1 at the left end and 3 at the right end) are "clean" Si=Si dimers. Again, the monohydride dimers also show a splitting into two well-resolved protrusions, while the "clean" dimers show only a single maximum. The dimers of monohydride appear 1.2 \AA lower than the "clean" dimers and therefore only 0.2 \AA higher than the substrate terrace.

Fig. 3a is a good example of how a slightly asymmetric tip can lead to misleading conclusions. Here, for example, we see that for dimers on the large terrace at right, the monohydride structure shows a clear splitting, while for dimers of the large terrace at left, the monohydride dimers appear lower, but the splitting cannot be easily observed. For the epitaxial dimers on these substrates, the situation is reversed, due to the 90 degree rotation of the dimer axis. Likewise, the corrugation between the dimers and along the dimer rows is different on these two terraces. The terrace at upper left shows corrugations of $0.18 \pm 0.03 \text{ \AA}$ and $0.50 \pm 0.03 \text{ \AA}$ parallel to and perpendicular to the dimer rows when measured over clean dimers, and no visible splitting of the monohydride structure. In contrast, the terrace at lower right shows corrugations of $0.11 \pm 0.03 \text{ \AA}$ and $0.71 \pm 0.05 \text{ \AA}$ parallel

to and perpendicular to the dimer rows when measured over clean dimers, and a dip in the center of the monohydride dimer which is 0.12 ± 0.02 Å below the maxima (which are almost directly over the H atoms). In effect, when the dimer corrugation measured along the dimer bond direction (perpendicular to the dimer rows) is large, the monohydride dimers show a splitting, while when the corrugation along the dimer bond direction is small (indicating a "double tip"), the splitting is not observed. Thus, the ability or inability to observe the splitting of the monohydride is clearly connected with the sharpness of the tip *when measured parallel to the dimer bond direction*, with sharp tips showing the splitting. An asymmetric tip might easily resolve the dimers along the rows while still not observing the splitting of the monohydride dimers, because these corrugations are along perpendicular directions. In general, a good test for the sharpness and symmetry of an STM tip on Si(001) is the magnitude of the corrugation measured along the two perpendicular directions of the Si(001) surface when measured on two separate terraces.

Because the contrast perpendicular and parallel to the dimer rows (approximately 0.7 Å and 0.2 Å, respectively) is small compared to the apparent height difference between monohydride and clean dimers (1.2 Å at -2 V bias), it can be difficult to see the monohydride structure clearly in a single grayscale image of fixed contrast, particularly when small sample-tip bias voltages are used during imaging. However, as the bias voltage is increased to larger negative sample voltages, the contrast between clean and monohydride dimers decreases. To study this contrast more quantitatively, the region shown in figure 1a was repetitively scanned over a range of bias voltages, and height profiles like that shown in fig. 1c were measured to determine the contrast. The results, shown in

fig. 4, demonstrate that at most bias voltages between -1.6 and -2.6 V, which are commonly used in STM experiments on Si(001), the monohydride appears to be more than 1 Å lower than the Si=Si dimers, and can even appear lower by more than the 1.36 Å step height of Si(001). The result of this "electronic contrast" is that regions of monohydride can easily be mistaken for surface vacancies, since vacancy defects and the monohydride structure have nearly the same height. As a result, for bias voltages between -1.6 and -2.6 V the height difference alone cannot be used to easily identify the monohydride structure; either the spatial symmetry of tunneling current within the unit cell must be used as auxiliary information, or else bias voltages of 3.0 Volts or greater must be used to distinguish between monohydride and simple vacancies. In studies of chemical vapor deposition, for example, the ability to make this distinction is particularly important because of the possibility of silicon etching through formation and desorption of SiH_x species at elevated temperatures, which would produce regions containing true vacancies.

As an example of where the height difference alone is not sufficient to identify a vacancy or monohydride structure, fig. 5a shows a region of the surface which was exposed to 0.2 L disilane and then annealed to 470 K. As described in another publication²⁴, this procedure produces small regions of the surface which at first appear like vacancy defects. (Also present are disilane dissociation fragments of the form $\text{SiH}_x(\text{ads})$, which appear as bright protrusions in this image.) However, either by height mapping using a grayscale shifted by 1 Å from that of fig. 5a, or by curvature mapping, the STM images reveal this apparent vacancy clearly contains dimers, and these dimers show a clear minimum at the center of the Si-Si bond. Fig. 5b shows the result of local curvature mapping,

showing how the dimer structure and also the splitting of the monohydride dimers can be observed. One particularly clear example of a dimer showing the splitting is outlined in fig. 5b. This demonstrates that the regions which appear like vacancies are in fact small regions of monohydride. Because they appear lower than the substrate by nearly the Si(001) step height, however, it is quite easy to mistakenly identify such regions as vacancies when in fact they are not.

On complex surfaces, the ability to identify the clean and monohydride dimers on a dimer-by-dimer basis is important in understanding the overall chemical processes occurring. For example, fig. 6a shows a Si(001) surface which has been exposed to 0.6 Langmuir Si_2H_6 and then annealed to 660 K. Again, because the difference in apparent height between the "clean" and monohydride structures is close to the 1.36 Å step height of Si(001), care must be taken to distinguish dimers of monohydride from vacancies. In this image, the tip was quite sharp and symmetric, so that dimers of the monohydride on both the lower (substrate) terrace and on the upper terrace (epitaxial islands) show the splitting for the monohydride dimers. Detailed analysis of images such as fig. 6a can be used to make "chemical maps" of the surface, as shown in fig. 6b. Here, ovals indicate "clean" dimers and small circles represent hydrogen atoms on dimers of the monohydride phase. Dark ovals and circles represent dimers of the substrate terrace, while light ovals and circles represent the epitaxial islands. Some regions in which the chemical composition could not be unambiguously determined have been left completely open. From the chemical map, one can more easily analyze the surface structure. For example, the chemical map clearly shows how dimers of the monohydride phase segregate into a separate phase, rather

than being randomly distributed across the surface. Likewise, one can see the regions of monohydride are comparatively isotropic in shape, while the epitaxial islands of silicon (with some monohydride dimers) are quite anisotropic, forming one-dimensional dimer strings. Further analysis, to be presented elsewhere²⁴, shows that the spatial distribution of hydrogen between epitaxial islands and even within dimers of a given epitaxial island is non-statistical. Our detailed analysis of the spatial distribution of hydrogen shows that this anisotropy is in fact opposite from that observed in two previous studies^{18, 23} of hydrogen on Si(001), underscoring the importance of proper identification of monohydride and clean dimer phases.

As described above, the origin of the height difference between monohydride and clean dimers is easy to understand based on a simple molecular orbital picture of the surface electronic structure, as shown in fig. 2. However, the detailed changes in the spatial distribution of tunneling current within the unit cell are more difficult to understand and have been controversial. Irrespective of its origin, we find that the splitting of the monohydride dimers at negative sample bias is a real, reproducible effect which is consistently observed with sharp, symmetric STM tips. We believe that the most likely reason for the inability to see this splitting is a dull or asymmetric tip. However, we also note that minimum at the center of the monohydride dimer is rather shallow, only about 0.12 Å below the two individual maximum within the unit cell. Thus, even a small degree of asymmetry in the tip or a high noise level could easily mask its presence.

CONCLUSIONS

We have demonstrated that dimers of the clean silicon can be distinguished from dimers of the monohydride structure (Si(001)-(2x1)H) based both on the apparent height difference at negative sample bias (probing filled surface states) and from the difference in spatial distribution of tunneling current within the unit cell. At most bias voltages used in STM studies, dimers of monohydride appear about 1.2 \AA higher than the "clean" dimers of the same terrace, and so are easily mistaken for vacancies. The height contrast between clean and H-covered dimers decreases as the bias voltage is increased, making it possible to distinguish monohydride dimers from vacancies. When imaged with sharp tips, each monohydride dimer shows two well-resolved protrusions 3.3 \AA apart, separated by a minimum approximately 0.11 \AA deep. On Si(001) surfaces which have been exposed to disilane and annealed to form small islands of epitaxial silicon, we are able to distinguish dimers of clean silicon and the monohydride structure on a dimer-by-dimer basis and find that the monohydride phase nucleates into nearly isotropic islands, while the silicon forms strongly anisotropic islands.

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Figure captions:

Figure 1(a): Si(001) surface after exposure to 0.6 L Si₂H₆ at 300 K, then annealed at 560K for 5 min. showing both clean dimers and monohydride dimers. Linear dimensions: 190 Å X 190 Å, V_s = -3.0 V, I_t = 0.5 nA;

(b): Enlarged view of area outlined by rectangular box in fig. 1a, showing that monohydride dimers appear lower and show a slight minimum at the dimer center. Linear dimensions: 31 Å X 52 Å, V_s = -3.0 V, I_t = 0.5 nA;

(c): Height profile measured along the line between the two arrows in (a), showing that at this bias monohydride dimers appear about 1 Å lower than Si=Si dimers, and that monohydride dimers show two protrusions across the dimer direction with a minimum at the center, while "clean" dimers show only a single maximum.

Figure 2: Simple molecular-orbital energy level diagrams for different structures on Si(001),

(a) electronic structure for bulk-terminated, unreconstructed Si(001);

(b) electronic structure after 2X1 dimer reconstruction;

(c) electronic structure after adsorption of two H atoms per dimer to form the monohydride phase.

Figure 3: STM image of Si(001) surface, including a monatomic step, after exposure to 0.6 L Si₂H₆ at 300 K and then annealed at 660K for 5 min. The tip is slightly asymmetric, producing different corrugation amplitudes on the two terraces as described in text.

(a) large-view image showing that monohydride phase is clearly visible on both substrate and on epitaxial islands. Linear dimensions: 270 Å X 340 Å. V_s = -1.9 V, I_t = 0.5 nA

(b) Enlarged view of rectangular region from (a), showing that monohydride dimers occur near the center of epitaxial dimer strings, appear 1.2 \AA lower than "clean" dimers, and show a minimum at the center of the dimer bond. Linear dimensions: $69 \text{ \AA} \times 131 \text{ \AA}$.

Figure 4: Apparent height difference between "clean" Si=Si dimers and monohydride dimers, obtained from repeated measurements over the area shown in fig. 1a at different bias voltages.

Figure 5: Height-mapped and curvature-mapped images of a Si(001) surface after exposure to $0.2 \text{ L Si}_2\text{H}_6$ at 300 K , then annealed at 470K for 2 min . Linear dimensions: $80 \text{ \AA} \times 80 \text{ \AA}$, $V_s = -2.0 \text{ V}$, $I_t = 0.5 \text{ nA}$.

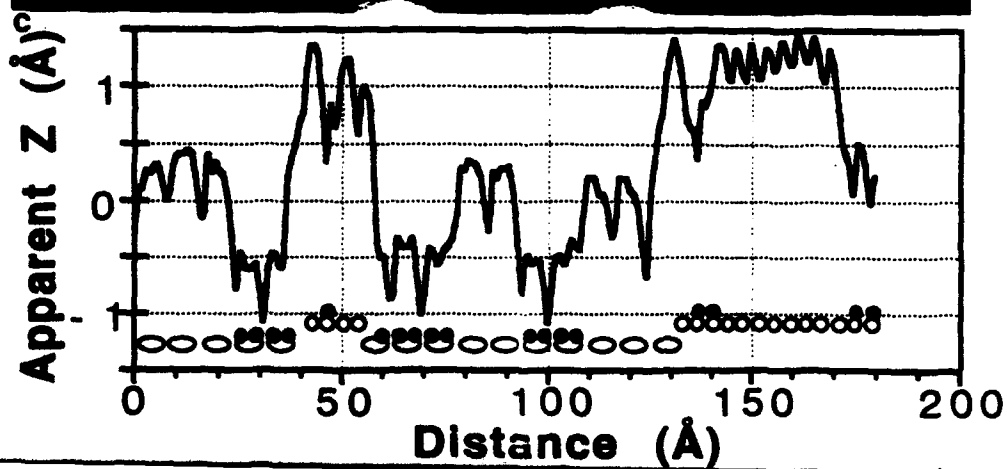
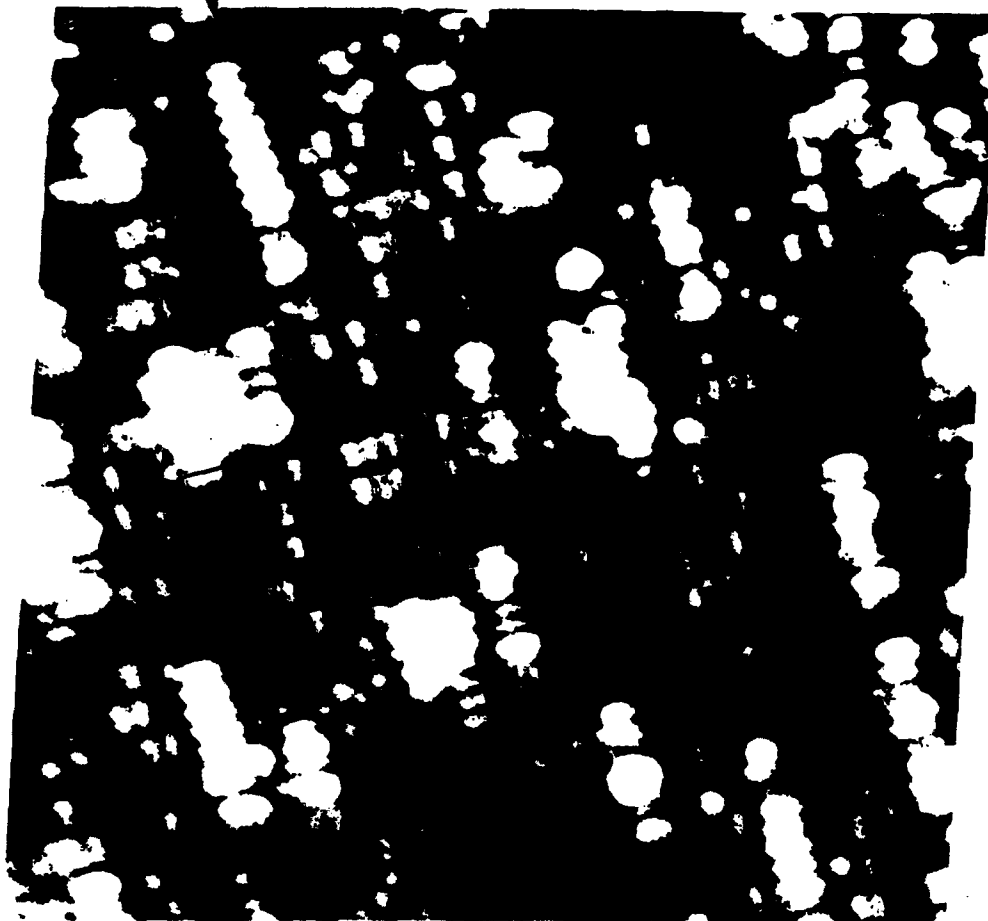
a) Height-mapped image: two unit cells are outlined with rectangular boxes; the upper cell is a clean dimer, while the lower appears like a vacancy.

(b): Curvature mapped image: The upper unit cell again appears like a clean dimer while the lower unit cell now reveals a dimer with its axis parallel to those of the substrate and the characteristic splitting typical of monohydride dimers.

Figure 6: "Chemical mapping" of mixed-phase surface containing clean and monohydride dimers.

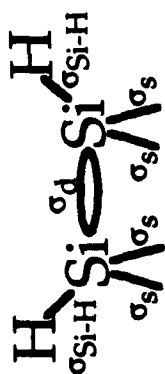
(a) STM image of Si(001) surface after exposure to $0.6 \text{ L Si}_2\text{H}_6$ at 300 K , then annealed at 660K for 5min , showing the monohydride phase on both the epitaxial layer and the substrate. Linear dimensions: $77 \text{ \AA} \times 139 \text{ \AA}$, $V_s = -1.9 \text{ V}$, $I_t = 0.5 \text{ nA}$.

(b) Chemical map corresponding to (a). The paired circles are monohydride dimers and ellipses are "clean" Si=Si dimers. The epitaxial layer uses open symbols, the substrate layer uses dark symbols.

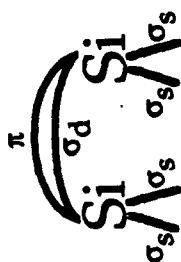


Wang et al.
Fig. 1

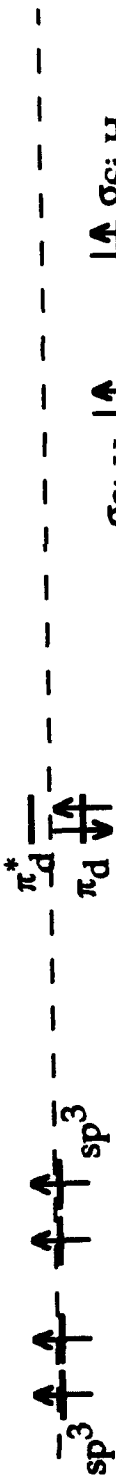
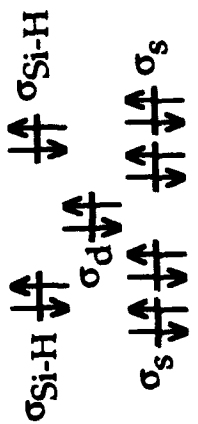
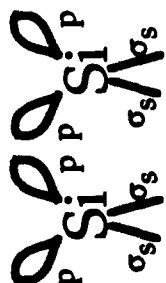
(c)



(b)

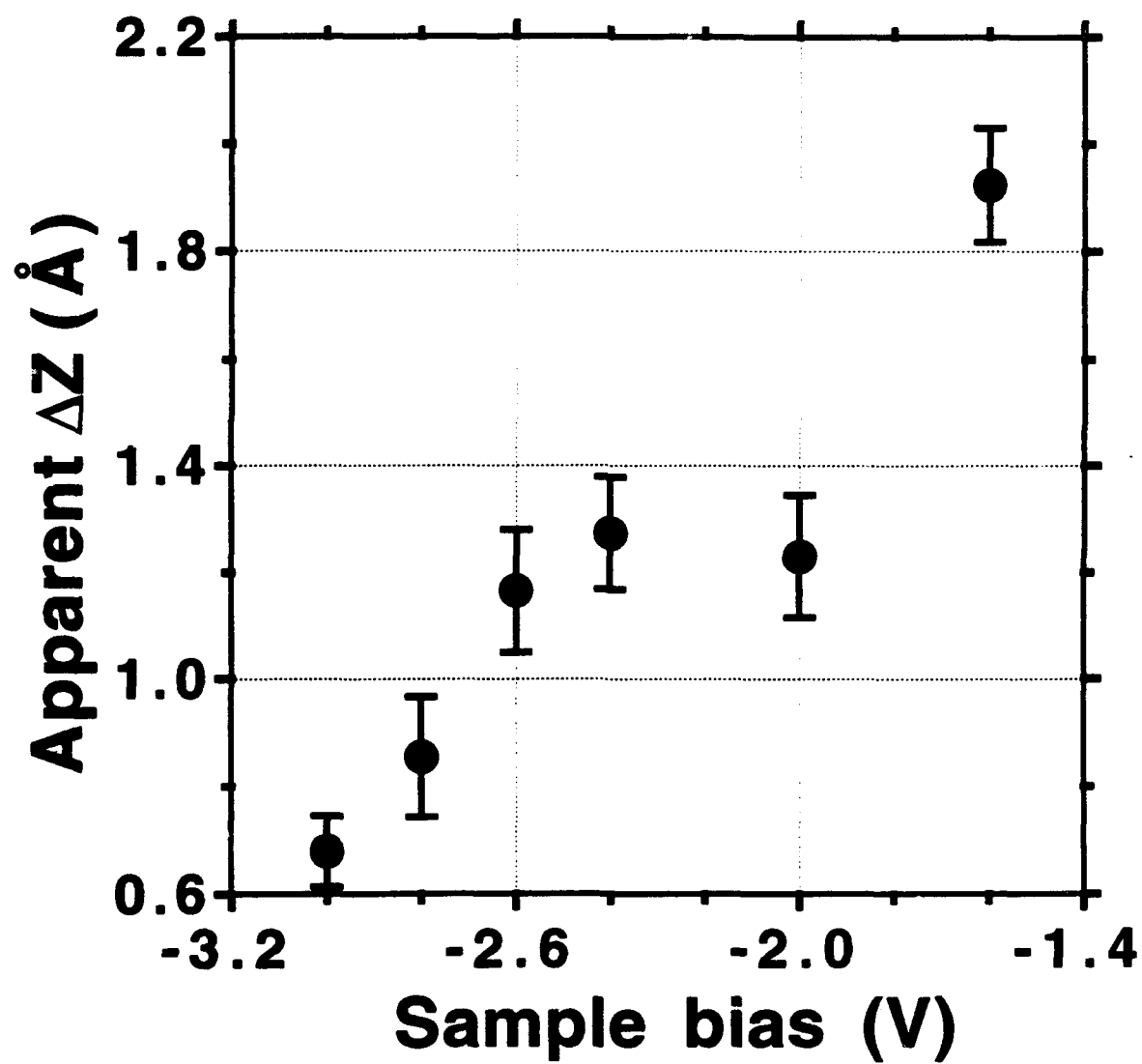


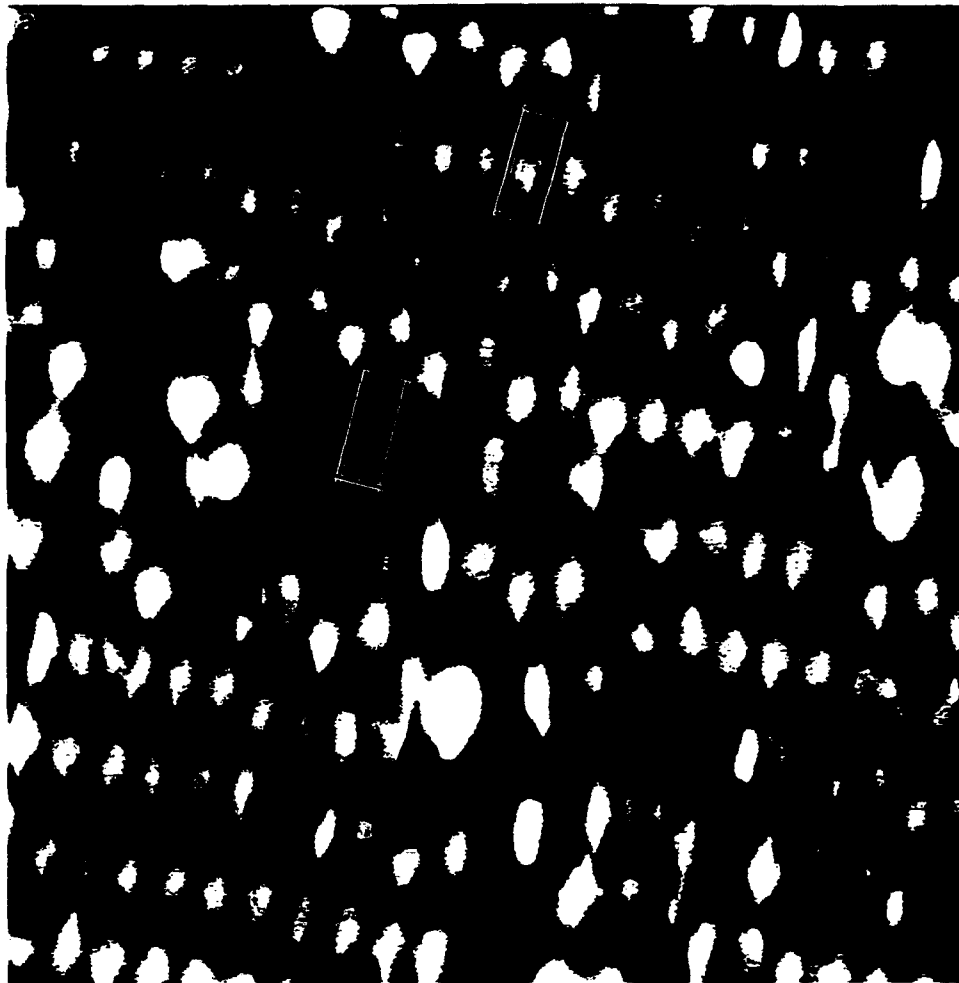
(a)





Wang et
Fig. 3





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